

## PATENT

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01/15/03

OFFICIAL

Docket Number: DN 99-100

Application of: Michael B. Freeman et al.

Serial No: 09/727,324

Group Art Unit: 1714

Filed: November 30, 2000  
(Priority to 14-Dec-99)

Examiner: C. Shosho

Title: POLYMERIC BINDER FOR WATER-RESISTANT INKJET INKSMail Stop FEE AMENDMENT  
Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

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DECLARATION UNDER 37 C.F.R. § 1.132

I, Michael Paul Hallden-Abberton, declare and say that:

1. I am a citizen of the United States of America, residing at 964 Whitney Lane, Maple Glen, Pennsylvania. I graduated in 1973 from the State University of New York at Potsdam located in Potsdam, NY, with a BA. Degree in Chemistry. I graduated in 1978 from Ohio State University, located in Columbus, Ohio, with a Ph.D. Degree in Organic Chemistry. Since 1978 I have been working in the field of polymer chemistry at the Rohm and Haas Company. Since 1999 I have been a Research Fellow (senior research chemist) in the Exploratory Polymer Research and Architectural and Functional Coatings Departments of Rohm and Haas Company. I have been granted 19 patents in the field of polymer chemistry and I am the author of 17 papers in the polymer chemistry and organic chemistry fields. I am familiar with the above-identified

CERTIFICATE OF TRANSMISSION

I certify that this paper, along with any referred to as being attached or enclosed, is being facsimile transmitted to (703) 872-9310 under 37 CFR § 1.8 on the date indicated below and is addressed to Commissioner for Patents, PO Box 1450, Alexandria, VA 22313-1450.

July 2, 2003  
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Karl Stauss  
Signature of Person Mailing Paper

KARL STAUSS  
Name of Person Mailing Paper

patent application Serial No. 09/727,324 and with the European patent application published as EP 590604, cited by the Examiner in an office action dated February 7, 2003.

2. Under my direction, a number of samples of polymeric binders were prepared on behalf of Rohm and Haas Company and supplied to Lexmark International, Inc. for preparation of inks comprising said binders and for testing of printing properties. The tests compared (a) the effectiveness of the binder samples to adhere pigment to paper substrates as applied in an ink jet ink formulation by an ink jet printer as tested by wet rub, highlighter rub and smear resistance, and (b) the ability to print without clogging the printer head nozzles (referred to hereafter as printer head reliability). The polymer emulsions were prepared according to the technique described in the above-identified patent application.

3. In order to show criticality of the claimed particle size and glass transition temperature, the examples below were prepared and tested. Example 1 is a repeat of Example 4 in the aforesaid patent application. This control sample was made because of new printing equipment used for testing purposes, and this example shows that the results are substantially similar to the old printing equipment used in the patent application. The following examples were prepared at sixty percent (60%) of the scale of the original patent application examples, all proportions being held to the original proportions on a per kilogram (/kg) of product basis.

#### Example 1

A sample of butyl acrylate (BA), methyl methacrylate (MMA), and methacrylic acid (MAA) polymer was prepared according to the procedure in Example 4 of the present patent application (as a repeat control example) except that the sample was prepared at a smaller size (60% of Example 4), using a monomer mixture which consisted of 390g deionized water, 16.9 g MAA, 397.9 g MMA, 881.3 g BA and 6.3 g SLS (at 28% solids). In this case, a reaction vessel containing 680 g deionized, buffered water (0.122 meq buffer/g water) and 1.8 g SLS (28.0%) was heated to 81°C. Then 69.0 g of the monomer mix with a 12 g water rinse was added to the vessel followed by 3.36 g NaPS dissolved in 30 g of water. This combination was held at 81°C for 10 minutes and then the remaining monomer mixture was added over 180 minutes along with

an additional 10.5 g SLS and a co-feed of 1.3 g NaPS in 60 g of water (added over 185 minutes). After the co-feed was completed, the reaction was held at 81°C for 30 minutes. Then the product was cooled, filtered and neutralized with the neutralization accomplished by combining 1200 g of un-neutralized product with 1003 g deionized water and brought to a pH of 8.5 with KOH. The resultant polymer had an average particle size of 287 nm with a particle size distribution ranging from 184 nm to 414 nm. The calculated T<sub>g</sub> was 0°C. The actual T<sub>g</sub> was measured using differential scanning calorimetry (DSC) and was -8°C. In an assessment of printability, a sample ink containing 3.0% by weight of the polymer was used to print 90 pages on a Lexmark desktop printer. On the 90<sup>th</sup> page of this print test, which was repeated four times, an average of 30 nozzles in the ink cartridge had misfired (178 nozzles continued to fire). Performance in terms of wet-rub smear or resistance to smearing by highlighter pens was excellent with little or no smearing evident. Note that Example 4 of the patent application used the procedure of Example 2 of the patent application unless otherwise noted.

#### Example 2

To show the effect of decreasing average particle size (within the invention), the procedure described in Example 1 above was repeated using a monomer mixture which consisted of 390g deionized water, 16.9 g MAA, 397.9 g MMA, 881.3 g BA and 6.3 g SLS (at 28% solids). In this case, a reaction vessel containing 680 g deionized, buffered water (0.122 meq buffer/g water) and 2.4 g SLS (28.0%) was heated to 81°C. Then 69.0 g of the monomer mix with a 12 g water rinse was added to the vessel followed by 3.36 g NaPS dissolved in 30 g of water. This combination was held at 81°C for 10 minutes and then the remaining monomer mixture was added over 180 minutes along with an additional 9.9 g SLS and a co-feed of 1.3 g NaPS in 60 g of water (added over 185 minutes). The sample was completed and neutralized as in Example 1 above. The resultant polymer had an average particle size of 255 nm with a particle size distribution ranging from 154 nm to 375 nm. The calculated T<sub>g</sub> was 0°C (actual T<sub>g</sub> was -9°C). In an assessment of printability, a sample ink containing 3.0% by weight of the polymer was used to print 90 pages on a Lexmark desktop printer. On the 90<sup>th</sup> page of this print test which was repeated four times, an average of 68 nozzles in the ink cartridge had misfired (140 nozzles continued to fire).

Performance in terms of wet-rub smear or resistance to smearing by highlighter pens was excellent with little or no smearing evident.

### Example 3

To show the effect of decreasing average particle size and low particle size range (outside the invention), the procedure described in the preceding paragraph was repeated using a monomer mixture which consisted of 390g deionized water, 16.9 g MAA, 397.9 g MMA, 881.3 g BA and 6.3 g SLS (at 28% solids). In this case, a reaction vessel containing 680 g deionized, buffered water (0.122 meq buffer/g water) and 3.9 g SLS (28.0%) was heated to 81°C. Then 69.0 g of the monomer mix with a 12 g water rinse was added to the vessel followed by 3.36 g NaPS dissolved in 30 g of water. This combination was held at 81°C for 10 minutes and then the remaining monomer mixture was added over 180 minutes along with an additional 8.4 g SLS and a co-feed of 1.3 g NaPS in 60 g of water (added over 185 minutes). The sample was completed and neutralized as in Example 1 above. The resultant polymer had an average particle size of 206 nm with a particle size distribution ranging from 121 nm to 302 nm. The calculated T<sub>g</sub> was 0°C (actual T<sub>g</sub> was -8°C). In an assessment of printability, a sample ink containing 3.0% by weight of the polymer was used to print 90 pages on a Lexmark desktop printer. On the 90<sup>th</sup> page of this print test which was repeated four times, an average of 156 nozzles in the ink cartridge had misfired (52 nozzles continued to fire).

### Example 4

To show the effect of continued decreasing average particle size and low particle size range (outside the invention), the procedure described in the preceding paragraph was repeated using a monomer mixture which consisted of 390g deionized water, 16.9 g MAA, 397.9 g MMA, 881.3 g BA and 6.3 g SLS (at 28% solids). In this case, a reaction vessel containing 680 g deionized, buffered water (0.122 meq buffer/g water) and 4.6 g SLS (28.0%) was heated to 81°C. Then 69.0 g of the monomer mix with a 12 g water rinse was added to the vessel followed by 3.36 g NaPS dissolved in 30 g of water. This combination was held at 81°C for 10 minutes and then the remaining monomer mixture was added over 180 minutes along with an additional 7.7 g SLS and a co-feed of 1.3 g NaPS in 60 g of water (added over 185 minutes). The sample was completed

and neutralized as in Example 1 above. The resultant polymer had an average particle size of 182 nm with a particle size distribution ranging from 88 nm to 273 nm. The calculated Tg was 0°C (actual Tg was -10°C). In an assessment of printability, a sample ink containing 3.0% by weight of the polymer was used to print 90 pages on a Lexmark desktop printer. On the 90<sup>th</sup> page of this print test which was repeated four times, an average of 181 nozzles in the ink cartridge had misfired (27 nozzles continued to fire).

#### Example 5

To show the effect of continued decreasing average particle size and low particle size range (outside the invention), the procedure described in the preceding paragraph was repeated using a monomer mixture which consisted of 390g deionized water, 16.9 g MAA, 397.9 g MMA, 881.3 g BA and 6.3 g SLS (at 28% solids). In this case, a reaction vessel containing 680 g deionized, buffered water (0.122 meq buffer/g water) and 6.0 g SLS (28.0%) was heated to 81°C. Then 69.0 g of the monomer mix with a 12 g water rinse was added to the vessel followed by 3.36 g NaPS dissolved in 30 g of water. This combination was held at 81°C for 10 minutes and then the remaining monomer mixture was added over 180 minutes along with an additional 6.3 g SLS and a co-feed of 1.3 g NaPS in 60 g of water (added over 185 minutes). The sample was completed and neutralized as in Example 1 above. The resultant polymer had an average particle size of 158 nm with a particle size distribution ranging from 77 nm to 231 nm. The calculated Tg was 0°C (actual Tg was -10°C). In an assessment of printability, a sample ink containing 3.0% by weight of the polymer was used to print 90 pages on a Lexmark desktop printer. On the 90<sup>th</sup> page of this print test which was repeated four times, an average of 207 nozzles in the ink cartridge had misfired (1 nozzle continued to fire).

#### Example 6

To show the effect of increasing Tg (within the invention), the procedure described in the preceding paragraph was repeated using a monomer mixture which consisted of 390g deionized water, 16.9 g MAA, 628.5 g MMA, 649.8 g BA and 6.3 g SLS (at 28% solids). In this case, a reaction vessel containing 680 g deionized, buffered water (0.122 meq buffer/g water) and 1.8 g SLS (28.0%) was heated to 81°C. Then 69.0 g of the monomer mix with a 12 g water rinse was

added to the vessel followed by 3.36 g NaPS dissolved in 30 g of water. This combination was held at 81°C for 10 minutes and then the remaining monomer mixture was added over 180 minutes along with an additional 10.5 g SLS and a co-feed of 1.3 g NaPS in 60 g of water (added over 185 minutes). The sample was completed and neutralized as in Example #1. The resultant polymer had an average particle size of 297 nm with a particle size distribution ranging from 190 nm to 435 nm. The calculated Tg was +20°C (actual Tg was +19°C). In an assessment of printability, a sample ink containing 3.0% by weight of the polymer was used to print 90 pages on a Lexmark desktop printer. On the 90<sup>th</sup> page of this print test which was repeated four times, an average of 52 nozzles in the ink cartridge had misfired (156 nozzles continued to fire). Performance in terms of wet-rub smear or resistance to smearing by highlighter pens was intermediate (not as good as Example 1 above, but better than an ink made without a binder).

#### Example 7

To show the effect of increasing Tg (outside the invention), the procedure described in the preceding paragraph was repeated using a monomer mixture which consisted of 390g deionized water, 16.9 g MAA, 729.5 g MMA, 548.6 g BA and 6.3 g SLS (at 28% solids). In this case, a reaction vessel containing 680 g deionized, buffered water (0.122 meq buffer/g water) and 1.8 g SLS (28.0%) was heated to 81°C. Then 69.0 g of the monomer mix with a 12 g water rinse was added to the vessel followed by 3.36 g NaPS dissolved in 30 g of water. This combination was held at 81°C for 10 minutes and then the remaining monomer mixture was added over 180 minutes along with an additional 10.5 g SLS and a co-feed of 1.3 g NaPS in 60 g of water (added over 185 minutes). The sample was completed and neutralized as in Example 1 above. The resultant polymer had an average particle size of 311 nm with a particle size distribution ranging from 198 nm to 456 nm. The calculated Tg was +30°C (actual Tg was +33°C). In an assessment of printability, a sample ink containing 3.0% by weight of the polymer was used to print 90 pages on a Lexmark desktop printer. On the 90<sup>th</sup> page of this print test which was repeated four times, an average of 30 nozzles in the ink cartridge had misfired (178 nozzles continued to fire). Performance in terms of wet-rub smear or resistance to smearing by highlighter pens was the worst of all samples in this series (not as good as Example 6 above).

Once the print quality was determined to be poor, highlighter resistance was not determined. The above Examples and test results are summarized in the following table:

Sample	Avg. Particle Size (nm)	Min. to Max. Particle Size (nm)	Tg (°C)	Highlighter Resistance	Print Quality (Nozzle Test)
<b>Particle Size Variations</b>					
Example 1	287	184-414	-8	Excellent	178/208 firing
Example 2	255	154-375	-9	Excellent	140/208 firing
Example 3	206	121-302	-8	N/A	52/208 firing
Example 4	182	88-273	-10	N/A	27/208 firing
Example 5	158	77-231	-10	N/A	1/208 firing
<b>Tg Variations</b>					
Example 1	287	184-414	-8	Excellent	178/208 firing
Example 6	297	190-435	19	Intermediate	156/208 firing
Example 7	311	198-456	33	Worst	178/208 firing

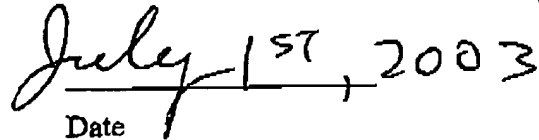
4. The above tests demonstrate criticality of particle size and Tg in the printer operability as measured by the number of nozzles that remain able to fire at the end of the printer test and the highlighter resistance property as measured by the relative optical appearance of the treated prints after rubbing with a highlighter as claimed in the above-identified patent application. In my opinion, the aforementioned criticality and superiority with respect to printer operability and highlighter resistance of the claimed invention is unobvious to one skilled in the art.

5. The undersigned declares further that all statements made herein of his own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patents issuing thereon.

Respectfully submitted,



Michael Hallden-Abberton

  
Date